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The University of Chicago.
Founded by JOHN D. ROCKEFELLER.

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On Nitroparaffin Salts and Acylated Derivatives of Hydroxylamine.

A DISSERTATION

SUBMITTED TO THE FACULTIES OF THE GRADUATE SCHOOLS OF ARTS, LITERATURE, AND SCIENCE, IN CANDIDACY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.

DEPARTMENT OF CHEMISTRY.

BY LAUDER W. JONES.

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On Salts of Nitroparaffins, and Acylated Derivatives of Hydroxylamine.

Of all the properties shown by the primary and secondary nitroparaffins, the two which seem to be the most characteristic are their tendency to form salts, and the peculiar power which they possess in the iso-form, either as salts or as esters, of producing oxidation-reactions. We are indebted chiefly to Nef[1] for our present conception of the salts. It was shown by him, that different constitutional formulæ must be assigned to the true nitro bodies and to their salts and esters, and that the metal or radical is bound to oxygen $\left(\begin{matrix} R—CH=N—O—M \\ \quad\quad\quad\quad\quad\quad \| \\ \quad\quad\quad\quad\quad\quad O \end{matrix}\right)$ and not to carbon ; the discovery of isophenylnitromethane by Hantzsch and Schultze[2] confirms the work of Nef.

It was stated in the paper on the nitroparaffins, that the action of acid chlorides on the salts would be studied ; that experiments with the yellow mercury salt obtained by the action of mercuric chloride on sodium isonitromethane, and attempts to synthesize esters of carbon dioxide oxime, R—O—N=C=O, would be continued. During the last three years, I have carried out further investigations along these lines under the direction of Dr. Nef, and now present my results in detail.[3]

I. THE ACTION OF ACID CHLORIDES ON SODIUM ISONITROETHANE AND SODIUM ISONITROMETHANE.

1. *The Action of Benzoyl Chloride on Sodium Isonitroethane.*

The sodium isonitroethane used in the following experi-

[1] Ann. Chem. (Liebig), **280**, 263. [2] Ber. d. chem. Ges., **29**, 699, 2251.

[3] A preliminary notice of my results, and a discussion of the formula proposed by Hantzsch for the nitroparaffin salts, were published by Dr. Nef in Ber. d. chem. Ges., **29**, 1218.

ments was prepared by adding sodium ethylate to an alcoholic solution of nitroethane. After filtering the salt, and washing thoroughly with alcohol and ether, it was carefully dried in a vacuum-desiccator to remove every trace of alcohol.

It was expected that the first product formed by the action of benzoyl chloride on sodium isonitroethane would be benzoylisonitroethane,

$$CH_3—CH=N—O—Na + C_6H_5—COCl =$$
$$\begin{matrix} & & \| & & \\ & & O & & \end{matrix}$$
$$CH_3—CH=N—O—CO—C_6H_5 + NaCl.$$
$$\begin{matrix} & & \| & & \\ & & O & & \end{matrix}$$

The reaction, however, is more complex in its nature, and benzoylisonitroethane undergoes a peculiar intramolecular oxidation, giving rise to an isomeric substance, the benzoyl ester of acethydroxamic acid.

$$CH_3—CH=N—O—CO.C_6H_5 \rightarrow CH_3—C\begin{matrix} O—H \\ \diagdown\!\!\diagup \\ N—O—COC_6H_5. \end{matrix}$$
$$\begin{matrix} & \| & \\ & O & \end{matrix}$$

This rearrangement furnishes a basis for the interpretation of the reaction. The benzoyl ester of acethydroxamic acid is a stronger acid than isonitroethane and decomposes sodium isonitroethane, setting free nitroethane, and forming the sodium salt of the benzoyl ester of the acethydroxamic acid,

$$CH_3—C\begin{matrix} O—Na \\ \diagdown\!\!\diagup \\ N—O—CO.C_6H_5. \end{matrix}$$

In the presence of benzoyl chloride, this salt is converted into triacylated hydroxylamine derivatives, neutral substances, which constitute the chief products of the reaction.

Essentially the same results are obtained, with slight variations in the relative amounts of acid and neutral products, whether the reacting substances are dissolved in water or suspended in absolute ether. In each of the following experi-

ments 20 grams of sodium salt were dissolved in 100 grams of water, and 28.8 grams of benzoyl chloride added; the table shows the relative quantities of acid and neutral products.

Experiment.	Soluble in $NaHCO_3$. Grams.	Soluble in NaOH. Grams.	Neutral Oil. Grams.
I.	6.5	3.2	12.3
II.	..	7.2	18.0
III.	6.5	7.0	16.5

Two experiments were performed, the substances being suspended in absolute ether: In Experiment I., 20 grams of sodium salt were suspended in 135 grams of absolute ether, and 28.8 grams of benzoyl chloride added; in Experiment II., 17.8 grams of sodium salt, 120 grams of absolute ether, and 25.0 grams of benzoyl chloride were used.

Experiment.	Soluble in $NaHCO_3$. Grams.	Soluble in NaOH. Grams.	Neutral. Grams.	Solid residue. Grams.
I.	4.7	3.5	19.3	13.5
II.	3.3	2.6	17.5	12.0

These two experiments were more favorable for a detailed study of the reaction than those carried out in water solution; they have been chosen as representative, and will be described in the account which follows.

17.5 grams of finely powdered sodium salt were suspended in 120 grams of absolute ether; the flask containing the mixture was placed in ice-water, and 25 grams (1 mol. = 25.7 grams) of benzoyl chloride were added in small portions. After standing a few minutes, the ether assumed a greenish hue, which finally passed into orange. The mixture was kept at 0° for two hours, and then allowed to stand at the temperature of the room, until the odor of benzoyl chloride was no longer noticeable.

The insoluble residue, removed by filtration, weighed 12 grams, and was composed chiefly of sodium chloride, with a small amount of sodium nitrite; no unchanged sodium isonitroethane was present.

The ether filtrate was placed in a distilling-bulb and subjected to distillation at reduced pressure; the distillate passed through a long, well-cooled condenser, and was caught in a

receiver surrounded by a freezing-mixture. When most of the ether had passed off, the pressure was diminished to 130 mm., and the temperature of the water-bath increased to 75°; at 85°, the thick, yellow oil in the distilling-bulb began to turn red, and to prevent further decomposition, the distillation was interrupted. The small amount of colorless liquid, which accumulated in the receiver, gave, on redistilling, 2 grams of nitroethane, boiling at 113°–114°, which was identified by its properties, and by converting it into ethylnitrolic acid.

The oil remaining in the distilling-bulb, which still possessed a strong odor of nitroethane, was redissolved in ether, and the ether solution extracted, first with sodium bicarbonate (A), and then with dilute sodium hydroxide (B) (containing 10 grams of the hydroxide in 100 grams of water). The ether containing the neutral portion (C) was washed carefully with water, dried with calcium chloride, and the ether then allowed to evaporate in a vacuum-desiccator.

A. Portion Soluble in Sodium Bicarbonate.

Benzoyl ester of acethydroxamic acid, $CH_3—C(=O)—N(H)—O—COC_6H_5$.

—After acidifying the bicarbonate solution with dilute sulphuric acid, it was extracted with ether; 3.3 grams of crystalline material were obtained on evaporating the ether, which proved to be a mixture of two substances, benzoic acid, and the benzoyl ester of *acethydroxamic acid*.

A separation of these two substances was easily effected by treatment with boiling ligroïn (40°–60°), which readily dissolves benzoic acid. By this method the solid (3.3 grams) was separated into 2 grams of benzoic acid (melting-point 119°–120°), and 1.3 grams of the benzoyl ester of acethydroxamic acid.

The latter exists in two forms: A part, 6.8 grams, was obtained by crystallizing from ether in large, well-developed crystals, melting at 98°–99°. The second form is more soluble in ether,

and can be precipitated from ether, after the other form has crystallized out, by means of low-boiling ligroïn, in flat, transparent crystals, melting at 69°–70°. After standing for several days, this form becomes opaque, and in the course of a week or two passes completely into the high-melting form.[1] It is possible that this low-melting form is a hydroximic acid, $CH_3—C(=N—O—CO.C_6H_5)—O—H$, and that the change, which it undergoes on standing, is due to a rearrangement to form a hydroxamic acid, $CH_3—C(=O)—NHOCO.C_6H_5$.

0.1257 gram, melting at 98°–99°, gave 0.2793 gram CO_2, and 0.0593 gram H_2O.

0.1282 gram gave 9 cc. N_2 at 14° and 749 mm.

	Theory for $C_9H_9NO_3$.	Found.
C	60.33	60.27
H	5.02	5.15
N	7.83	8.16

Properties of the Benzoyl Ester of Acethydroxamic Acid.—It is readily soluble in alcohol, less soluble in chloroform, or ether, sparingly soluble in cold water, and almost insoluble in ligroïn, and benzol.

Towards alkalies it is quite sensitive, and is readily decomposed by them into benzoic acid and acethydroxamic acid, $CH_3—C(=O)—N—HOH$. Even boiling water causes the same decomposition, but much less readily. On heating, it is completely decomposed; benzoic acid, methyl isocyanate, and a brown residue are formed.

Sodium Salt, $CH_3—C(=N—O—CO.C_6H_5)—O—Na$.—By adding so-

1 By adding acid to a water solution of the sodium salt of the form melting at 98°–99°, and extracting with ether, a mixture of the two forms is obtained.

dium ethylate to an alcoholic solution of the acid, and precipitating with absolute ether, a white, crystalline salt was obtained.

0.2582 gram gave 0.0843 gram Na_2SO_4.

	Theory for $C_9H_8NO_3Na$.	Found.
Na	11.43	11.46

This salt is readily soluble in water, and from this solution a white, non-crystalline silver salt can be precipitated by silver nitrate.

Synthesis of the Benzoyl Ester of Acethydroxamic Acid from Acethydroxamic Acid.—In order to establish the identity of the substance obtained from nitroethane, with the benzoyl ester of acethydroxamic acid, it was necessary to prepare this compound synthetically. 4 grams of acethydroxamic acid, $CH_3—C\begin{matrix}O\\ \diagup\!\!\diagdown\\ NHOH\end{matrix}$, (melting-point 88°–89°), prepared according to the method described by Miolati[1], were dissolved in 50 grams of water, and neutralized with 3 grams of potassium hydroxide in 25 grams of water. To this solution, well cooled, 7.5 grams of benzoyl chloride were added in small portions, shaking thoroughly after the addition of each portion. In a few minutes a dense, crystalline mass accumulated. This was collected on a filter, and pressed on a clay plate to remove water, and some unchanged benzoyl chloride. The dry product was treated with boiling ligroïn, which took up a small amount of benzoic acid.

This crude product (6.5 grams) was dissolved in ether. On standing, large, transparent crystals, melting at 98°-99°, were formed, which were identical in every respect with the substance obtained from nitroethane.

0.1796 gram, melting 98°–99°, gave 0.3975 gram CO_2, and 0.0842 gram H_2O.

0.2423 gram gave 16.9 cc. N_2 at 18° and 742.7 mm.

[1] Ber. d. chem. Ges., **25**, 700.

	Theory for $CH_3-C\overset{O}{\underset{NHOCO.C_6H_5}{<}}$.	Found.
C	60.33	60.36
H	5.02	5.20
N	7.83	7.90

In this case, also, two forms were observed. Of the 6.5 grams, 4.6 grams melted at 98°–99°, while 1.8 grams separated in flat crystals, melting at 69°–70°.

The absolute identity of the substance obtained from nitroethane (melting-point 98–99°), with the benzoyl ester of acethydroxamic acid, is established by the identity of the crystalline forms.

For the following crystallographic data, I am indebted to Mr. Zirngiebl, who kindly carried out the measurements of these two substances in Prof. Groth's laboratory at Munich.

Crystal system: monoclinic.

$a : b : c = 1.4623 : 1 : 1.4545$

$\beta = 94° 41'$

The forms which were observed are: 001, 110, 101, $11\bar{1}$, 100; the last two are sometimes wanting.

$001 : 100 = 85° 19'$

$001 : 101 = 42° 31'$

$110 : \bar{1}10 = 68° 43'$

Cleavage completely in 001.

The plane of the optical axes $\perp$ 010.

B. Portion Soluble in Sodium Hydroxide.

The solution in sodium hydroxide possessed an intense red color, which disappeared on acidifying with dilute sulphuric acid, and was due, as will be shown, to the presence of salts of ethylnitrolic acid. By means of ether 2.6 grams of crystalline material were extracted. This solid proved to be a mixture of the following substances:

	Grams.
Benzoic acid,	1.9
Benzoyl ester of benzhydroxamic acid, $C_6H_5-C\overset{O}{\underset{NHO.CO.C_6H_5}{<}}$,	0.4

Benzoyl ester of acethydroxamic acid, $CH_3—C(=O)—NHOCO.C_6H_5$, traces.

Ethylnitrolic acid $CH_3—C(=NO_2)—N—O—H$, traces.

A separation of these substances was accomplished as follows: The entire residue (2.6 grams) was dissolved in the smallest possible amount of sodium hydroxide, and carbon dioxide conducted into the solution until no more benzoyl ester of benzhydroxamic acid (dibenzhydroxamic acid) separated. This substance was removed by filtration, and extraction with ether. Recrystallized from alcohol, it separated in fine needles, melting at 158°–159°. A portion was converted into the potassium salt, and this, by boiling with water, into diphenylurea (melting at 235°–236°).

A nitrogen determination was also carried out.

0.2968 gram gave 15.1 cc. N_2 at 16.5° and 756.8 mm.

	Theory for $C_{14}N_{11}NO_3$.	Found.
N	5.80	5.90

The filtrate was acidified, and the benzoic acid which separated, collected on a filter and dried. It melted at 117°–118°, and contained traces of the benzoyl ester of acethydroxamic acid.

The acidified solution, from which the benzoic acid had been removed, was neutralized with sodium hydroxide; to the deep-red solution a few drops of benzoyl chloride were added, and the mixture shaken until a yellow crystalline solid deposited. After recrystallizing from boiling alcohol, this solid melted at 134°–135°, and was identical with the benzoyl ester of ethylnitrolic acid, $CH_3—C(=NO_2)—N—O—CO.C_6H_5$, which melts at 135°. 0.4 gram was obtained.

These substances are undoubtedly formed by the decomposition of the neutral portion in the presence of sodium hydroxide. The formation of ethylnitrolic acid is explained by the presence of the benzoyl ester of ethylnitrolic acid.

$CH_3—C(NO_2)(NOCOC_6H_5)$. When benzoyl chloride acts on sodium isonitroethane in water solution, larger amounts of this benzoyl compound are formed, and crystallize from the neutral oil on standing. Its presence is to be explained by a decomposition of sodium isonitroethane, with formation of nitrous acid; the green color, which the ether solution first assumes, points to this decomposition. Nitrous acid reacts with sodium isonitroethane to form ethylnitrolic acid, which is a stronger acid than isonitroethane, and decomposes sodium isonitroethane, forming the sodium salt of ethylnitrolic acid. This reacts with benzoyl chloride to form the benzoyl ester of ethylnitrolic acid. The formation of dibenzhydroxamic acid, $C_6H_5CO.NHOCOC_6H_5$, and the benzoyl ester of acethydroxamic acid will be explained, when the nature of the neutral portion is discussed.

C. Neutral Portion.[1]

Benzoyl Ester of Benzoylacethydroxamic Acid, $CH_3—C(O—COC_6H_5)(NOCOC_6H_5)$, and *α-Benzoyl-β-acetylbenzoylhydroxylamine*, $(CH_3—CO)(C_6H_5—CO)N.O—CO—C_6H_5$.

After the ether and volatile portions had passed off, 17.5 grams of thick, reddish oil remained. When the amount of material taken is compared with the amount recovered, it becomes apparent that considerable loss has occurred.

	Taken. Grams.		Found. Grams.
Sodium isonitroethane,	17.8	Neutral,	17.5
Benzoyl chloride,	25.0	Acid,	5.9
		Solid residue,	12.0
	42.8	Nitroethane,	2.0
			37.4

Loss = 5.4 grams.

[1] The neutral oil is not, as was at first supposed, a mixture containing "Tribenzhydroxylamine," $C_6H_5C(OCOC_6H_5)(NOCOC_6H_5)$, as one of its ingredients, but a mixture of the two isomers given above. *Vide* Ber. d. chem. Ges., **29**, 1218.

As no evolution of gas occurred, this loss must have been due to volatile liquid, and in view of the fact that nitroethane was recovered, and that the oil still possessed a strong odor of nitroethane, almost the entire loss must be attributed to regenerated nitroethane, except perhaps slight losses which occurred in extracting with sodium bicarbonate and sodium hydroxide.

The regenerated nitroethane would, on this basis, amount in all to 7.4 grams (5.4 grams + 2.0 grams), which is a little more than half of the nitroethane used.

7.4 grams of nitroethane = 9.5 grams of sodium isonitroethane.

One-half of the sodium salt used, 17.8 = 8.9 grams.

Properties of the Oil.—This oil showed no signs of solidifying in a freezing-mixture, and even after an exposure of several weeks to the extremest cold of winter weather, only a slight deposit was formed, and this redissolved on attempting to separate it from the oil.

It cannot be distilled, even under diminished pressure, without undergoing complete decomposition, with the formation of benzoic acid, acetic acid, an isocyanate, and a brown, non-volatile residue.

On warming a few drops of the oil with dilute alkali, it is decomposed; dilute sulphuric acid precipitates benzoic acid, and the acidified solution gives an intense reaction with ferric chloride, indicating the presence of hydroxamic acids.

The behavior of the oil towards concentrated hydrochloric acid, its behavior towards alcoholic potash, and an analysis show that it is a triacylated hydroxylamine derivative, to which the empirical formula, $(CH_3CO)(C_6H_5CO)_2ON$, must be assigned.

Behavior towards concentrated Hydrochloric Acid.—The oil is decomposed by concentrated hydrochloric acid into benzoic acid, acetic acid, and hydroxylamine hydrochloride, with traces of ammonium chloride.

5.0 grams were heated with 2–3 volumes of acid for two hours at 100° in a sealed tube. No pressure was observed on opening the tube.

The benzoic acid was filtered, washed once with ice-water, dried, and weighed. It was found to weigh 4.1 grams, while 4.3 grams is the amount calculated for $(CH_3CO)(C_6H_5CO)_2ON$.

The filtrate was diluted with water to a volume of 250 cc., and distilled until two-thirds of this volume had passed into the receiver. This distillate was treated with silver carbonate, heated to boiling, filtered, and evaporated to dryness on a water-bath. In this way 1.0 gram of silver acetate was obtained, which, after recrystallizing from hot water, and washing with absolute alcohol to remove traces of silver benzoate, gave the following figures on analysis:

0.1120 gram gave 0.0722 gram Ag.

	Theory for $CH_3—COOAg$.	Found.
Ag	64.66	64.46

The hydrochloric acid solution, which remained in the distilling-bulb, was evaporated to dryness in an evaporating-dish over a water-bath; 0.8 gram of the solid residue remained, consisting chiefly of hydroxylamine hydrochloride, with traces of ammonium chloride. It reduced Fehling's solution, and was converted into acetoxime; volatile, prismatic crystals were obtained, melting at 59°–60°.

Analysis.—The neutral oil, carefully washed with sodium bicarbonate and sodium hydroxide, and freed from volatile substances by standing *in vacuo* for two weeks, gave the following figures on analysis:

0.1658 gram gave 0.4175 gram CO_2, and 0.0690 gram H_2O.

0.1307 gram gave 0.3282 gram CO_2, and 0.0575 gram H_2O.

0.3407 gram gave 13 cc. N_2 at 21° and 748 mm.

	Theory for $(CH_3CO)(C_6H_5CO)_2ON$.	Found. I.	II.	III.
C	67.84	68.66	68.48	....
H	4.62	4.62	4.88	....
N	4.92	....	....	4.29

Considering the nature of the oil, and its method of preparation, the figures obtained agree well with the theory.

Behavior of the Oil towards Alcoholic Potash.

6.2 grams were dissolved in a few cubic centimeters of alco-

hol, and, after cooling the solution, 2.3 grams of potassium hydroxide (calculated 2 mol. = 2.4 grams), dissolved in a few grams of alcohol, were added. Almost immediately a crystalline salt formed, which increased on standing; after five minutes this salt was filtered from the deep-red alcoholic solution. It weighed 3.7 grams, and was composed of the potassium salts of benzoic acid and of the benzoyl ester of benzhydroxamic acid, $C_6H_5—C\begin{matrix}OK\\ \diagdown\\ \diagup\\ NOCOC_6H_5\end{matrix}$.

A separation of these two acids was accomplished by dissolving the mixture of the salts in water, and passing carbon dioxide through the solution. Thus 1.0 gram of the benzoyl ester of benzhydroxamic acid, melting at 158°–159°, was precipitated. It was also identified by converting it into diphenyl urea. On acidifying the filtrate, and extracting with ether, 1.6 grams of benzoic acid (melting-point 119°–120°) were obtained.

The original alcoholic solution was diluted with water and extracted with ether. 2.7 grams of the ethyl benzoate, boiling at 209°–212°, were obtained on distilling.

The solution was then acidified with dilute sulphuric acid, and extracted with ether. A solid, crystalline residue remained on evaporating the ether, which, recrystallized from ether and low-boiling ligroïn, gave 0.1 gram of the benzoyl ester of acethydroxamic acid, melting at 98°–99°, and 0.4 gram, melting at 69°–70°.

The presence of hydroxamic acids could be shown in the remaining solution by means of ferric chloride.

The results may be summed up as follows:

6.2 grams of oil gave:

	Grams.
Benzoyl ester of benzhydroxamic acid,	1.0
Benzoyl ester of acethydroxamic acid,	1.4
Benzoic acid,	1.6
Ethyl benzoate,	2.7

The formation of the benzoyl ester of acethydroxamic acid, $CH_3—CO.NH.CO.C_6H_5$, and benzoic acid (partially as ethyl

benzoate), can only be explained by the presence of the benzoyl ester of benzoylacethydroximic acid, $CH_3—C(O.CO.C_6H_5)=NO.CO.C_6H_5$, in the neutral oil. If the oil were made up entirely of this substance, it is impossible to account for the formation of the benzoyl ester of benzhydroxamic acid, $C_6H_5CONH.OCO.C_6H_5$. If, however, it is assumed that a triacylated hydroxylamine, constituted according to the true hydroxylamine type, *viz.*, $(CH_3CO)(C_6H_5CO)N—O—CO.C_6H_5$, is also present, the formation of the benzoyl ester of benzhydroxamic acid becomes explicable, for of two groups bearing the same relation to the nitrogen atom, the acetyl group would be more readily affected by alcoholic potash than the benzoyl group.

The decomposition may be expressed thus :

$$CH_3—\overset{\overset{O}{\|}}{C}—OH. \qquad C_6H_5—\overset{\overset{O}{\|}}{C}—\overset{\overset{H}{|}}{N}—O—COC_6H_5.$$

In order to establish the correctness of this interpretation, it was necessary to study the action of benzoyl chloride on the sodium salt of the benzoyl ester of acethydroxamic acid, $CH_3—C(ONa)=NOCOC_6H_5$.

The Action of Benzoyl Chloride on the Sodium Salt of the Benzoyl Ester of Acethydroxamic Acid.

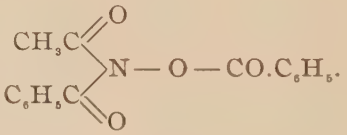
4.2 grams of the sodium salt, prepared as described above, were suspended in 38 grams of absolute ether, and 2.7 grams of benzoyl chloride (slightly less than 1 molecule) were added. The action commenced at once, and at the end of two days was complete.

The sodium chloride (1.2 grams) was filtered, and the ether solution evaporated ; a thick, colorless, syrupy oil remained in the evaporating-dish, weighing 5.4 grams. After standing for two weeks, exposed to the coldest winter temperature,

the oil showed signs of solidifying, and at the end of three weeks, the crystalline magma was transferred to a clay plate. The solid, freed from oil in this way, amounted to 2.5 grams. It was redissolved in a small quantity of ether, and warm ligroïn added, when, on cooling, it was deposited in large, transparent, well-developed crystals, melting at 68°–69°.

The oil was extracted from the pieces of clay plate by boiling ether; on evaporating the ether, a thick, oily substance remained, which showed no signs of solidifying after standing four weeks.

α-Benzoyl-β-acetylbenzoylhydroxylamine,



The solid, melting at 68°–69°, is a neutral substance, insoluble in alkalies, but decomposed by them quite readily. It is easily soluble in alcohol and ether, quite soluble in boiling ligroïn, sparingly soluble in cold ligroïn, and insoluble in water.

0.1327 gram gave 0.3307 gram CO_2, and 0.0560 gram H_2O.
0.1473 gram gave 6.8 cc. N_2 at 20° and 743.7 mm.

	Theory for $C_{16}H_{13}NO_4$.	Found.
C	67.84	67.95
H	4.62	4.68
N	4.94	5.15

The correctness of the formula assigned is shown by the behavior of the solid towards alcoholic potash, and more conclusively by its synthesis from the potassium salt of the benzoyl ester of benzhydroxamic acid and acetyl chloride, which will be considered later.

Behavior towards Alcoholic Potash.

The solid isomer is decomposed on treatment with alcoholic potash almost completely into the benzoyl ester of benz-

hydroxamic acid, $C_6H_5—C\begin{matrix}=O\\ \diagdown NHOCOC_6H_5\end{matrix}$, and acetic acid (or acetic ether). Not a trace of the benzoyl ester of acethydroxamic acid, $CH_3—C\begin{matrix}=O\\ \diagdown NHOCOC_6H_5\end{matrix}$, could be found.

1 gram of the crystalline isomer (melting-point 68°–69°) was dissolved in 20 grams of alcohol, and treated with alcoholic potash (0.4 KOH equivalent to 2 mols.). The crystalline salt which separated was filtered (0.4 gram), dissolved in water, and treated with carbon dioxide. In this way 0.38 gram of the benzoyl ester of benzhydroxamic acid, melting at 159°–160°, was obtained. It was identified by conversion into diphenylurea. The alcoholic filtrate was diluted with water, and extracted with ether. On distilling the ether extract, very small quantities of acetic ether, and benzoic ether were recognized by their odors. The diluted alcoholic solution was then acidified with dilute sulphuric acid; from this solution ether extracted 0.45 gram of the benzoyl ester of benzhydroxamic acid, containing traces of benzoic acid. This amount (0.45 gram), redissolved in sodium hydroxide and precipitated by carbon dioxide, gave 0.4 gram of pure acid, melting at 158°.

The acidified solution, from which these substances had been extracted, gave a reaction with ferric chloride for benzhydroxamic acid, $C_6H_5—CO.NHOH$, which was formed by the further decomposition of the benzoyl ester of benzhydroxamic acid; this explains the presence of traces of benzoic acid and benzoic ether.

In all, 0.76 gram of the benzoyl ester of benzhydroxamic acid were obtained instead of 0.85 gram, the calculated amount.

Benzoyl Ester of Benzoylacethydroximic Acid,

$$CH_3—C\begin{matrix}\diagup O—CO.C_6H_5\\ \diagdown N—O—CO—C_6H_5\end{matrix}.$$

The oily isomer obtained in the above reaction shows a

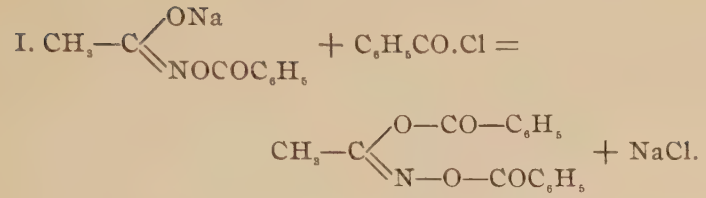
totally different behavior towards alcoholic potash. It is decomposed almost entirely into the benzoyl ester of acethydroxamic acid, $CH_3—C{=}O.NH.O.COC_6H_5$, and benzoic acid (or ethyl benzoate), which establishes the constitutional formula assigned. 0.9 gram of the oily isomer, treated with alcoholic potash (0.35 gram KOH in 17 grams alcohol) in exactly the same manner as the solid isomer, gave the following results:

		Gram.
Benzoyl ester of acethydroxamic acid,	$CH_3—C(=O)NHOCOC_6H_5$	0.5
Ethyl benzoate,	$C_6H_5.COOC_2H_5$	0.3
Benzoic acid,	C_6H_5COOH	trace
Benzoyl ester of benzhydroxamic acid,	$C_6H_5—C(=O)NHOCOC_6H_5$	0.08

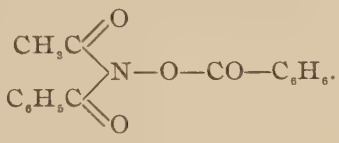
The formation of this last substance is to be accounted for by the presence of some of the solid isomer dissolved in the oil.

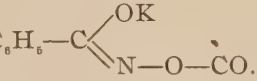
The neutral oil obtained from sodium isonitroethane, therefore, behaves in every respect as a mixture of almost equal quantities of these two isomers. It is not strange that this oil has resisted all attempts to solidify it, when we consider its method of preparation, and the fact that it contains slight impurities, such as ethyl benzoate and nitroethane. Furthermore, the product obtained by the action of the sodium salt of pure benzoyl ester of acethydroxamic acid and benzoyl chloride solidified but partially, and then only after an exposure of three weeks to extreme cold, accompanied by the usual scratching to facilitate crystallization.

It is only possible to explain the formation of the two isomers from the sodium salt of benzoyl ester of acethydroxamic acid and benzoyl chloride, by assuming that two processes are taking place side by side; namely, direct replacement of the metal by the benzoyl group, and the addition of benzoyl chloride to the sodium salt, with subsequent loss of sodium chloride.



By loss of sodium chloride the last product becomes



In order to establish the correctness of this explanation, the following experiment was carried out: Acetyl chloride was allowed to act on the potassium salt of the benzoyl ester of benzhydroxamic acid, 

It is evident that if addition does occur, the addition-product formed in this case must be identical with the solid isomer (melting-point 68°–69°) obtained by the addition of benzoyl chloride to the sodium salt of the benzoyl ester of acethydroxamic acid. This conclusion is borne out by experiment.

The Action of Acetyl Chloride on the Potassium Salt of the Benzoyl Ester of Benzhydroxamic Acid, —The benzoyl ester of benzhydroxamic acid used was pre-

pared according to Lossen's[1] method from hydroxylamine and benzoyl chloride.

11 grams of the potassium salt were suspended in absolute ether, and treated with 3.1 grams (1 mol.) of acetyl chloride. In twelve hours the action was complete. After removing the sodium chloride, the ether solution was placed in a glass evaporating-dish and the ether evaporated *in vacuo*. Thus, 8.2 grams of solid, crystalline material, with traces of oil, were obtained. The oil was removed by placing the solid on a clay plate, and was not investigated. The solid was crystallized as follows: Boiling ligroïn (40°–60°) dissolved it, with the exception of 0.5 gram of regenerated benzoylhydroxamic acid. On cooling, the ligroïn solution was filled with radiating groups of long, needle-shaped crystals, and at the same time short, thick, transparent crystals formed on the sides of the crystallizing flask. After filtering, these crystals were separated by selection. 3.7 grams of needle-shaped crystals, melting at 84°–85°, and 1.7 grams of transparent crystals, melting at 68°–69°, were obtained.

Solid Melting at 68°–69°.—This substance is identical in every respect with α-benzoyl-β-acetylbenzoylhydroxylamine, $\begin{matrix} CH_3CO \\ C_6H_5CO \end{matrix}\!\!>\!N—O—CO.C_6H_5$, obtained from the benzoyl ester of acethydroxamic acid.

0.1443 gram gave 0.3583 gram CO_2, and 0.0610 gram H_2O.
0.2545 gram gave 11.2 cc. N_2 at 22° and 753.8 mm.

	Theory for $C_{16}H_{13}NO_4$.	Found.
C	67.84	67.75
H	4.62	4.69
N	4.94	4.96

Behavior towards Alcoholic Potash.—0.9 gram dissolved in 17 grams of alcohol, and treated with a solution of potassium hydroxide, containing 3.5 grams, gave 0.7 gram of the benzoyl ester of benzhydroxamic acid, $C_6H_5C\!\!<\!\!\begin{matrix} O \\ NHOCOC_6H_5 \end{matrix}$; calculated 0.76 gram.

[1] Ann. Chem. (Liebig), **161**, 344.

A crystallographic comparison of crystals of this preparation with those obtained from the benzoyl ester of acethydroxamic acid and benzoyl chloride was carried out in Prof. Groth's laboratory at Munich by Mr. Zirngiebl, to whom I wish to express my obligation for his kindness. The complete identity of the two specimens is established.

Crystal system : monoclinic.

$$a : b : c = 1.3064 : 1 : 1.0390.$$

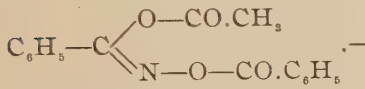
$$\beta = 107°22'.$$

The forms observed are : 010, 100, 001, $11\bar{1}$, $10\bar{1}$.

001	: 100	=	72°38′
$\bar{1}11$	: $\bar{1}00$	=	70°36′
$\bar{1}11$	: $\bar{1}\bar{1}1$	=	87°59′

Cleavage 001. Plane of the optical axes ⊥ 010.

Benzoyl Ester of Acetylbenzhydroximic Acid,

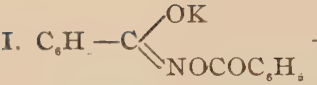


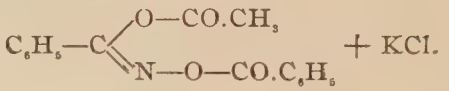
.—The solid, melting at 84°–85°, obtained in the same reaction, is formed by the direct replacement of the metal by the acetyl group. It is a neutral substance, soluble in ether, and alcohol, very slightly soluble in cold ligroïn, quite readily in warm ligroïn, and insoluble in water.

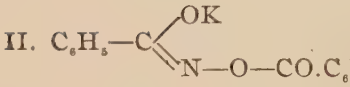
0.0602 gram gave 0.1494 gram CO_2, and 0.0265 gram H_2O.
0.2240 gram gave 9.7 cc. N_2 at 25° and 749.7 mm.

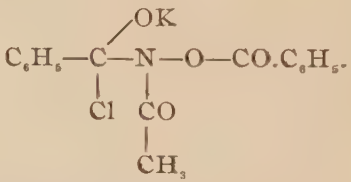
	Theory for $C_{16}H_{13}NO_4$.	Found.
C	67.84	67.68
H	4.62	4.88
N	4.94	4.79

The following equations will explain the formation of these substances :

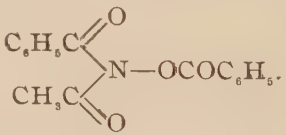
I. 



II. 



This addition-product loses potassium chloride giving



These reactions seem to throw some light upon the nature of the triacylated hydroxylamine derivatives in general. It has been established that compounds of this class exist in more than one form ; in no case, however, in more than three forms. Lossen[1] has preferred to regard them as physical isomers, not, however, denying the possibility of considering them as space isomers. Hantzsch and Werner suggested the possibility of interpreting them from the standpoint of geometrical isomerism, depending upon the presence of an oxime grouping. Werner[2] has since established the presence of such isomeric relations among the hydroximic acid derivatives, as, for example, α- and β-ethylhydroximic acid, which he showed to be related as *syn* and *anti* forms,

[1] Ann. Chem. (Liebig), **186**, 1 ; **252**, 170 ; **265**, 176 ; **281**, 169.
[2] Ber. d. chem. Ges., **25**, 27 ; **26**, 1562, 1567 ; **29**, 1153.

This, however, accounts for only two forms, and in some cases three are known. It has often been suggested that the third form may correspond to a true hydroxylamine type, $\begin{matrix}RCO\\RCO\end{matrix}\!\!>\!N—O—COR$; but experimental evidence was lacking to confirm this view. The results, presented above, prove conclusively that compounds of this type can exist. It still remains to be determined whether even this explanation is sufficient to account for all the cases of isomerism, and the many intricate relations observed in the study of the hydroxamic and hydroximic acids.

Explanation of the Reaction of Benzoyl Chloride with Sodium Isonitroethane.

Having considered this reaction in all its details, it is now possible to sum up the results, and to formulate the course of the action in the following equations. By the direct replacement of the metal by benzoyl, a derivative of isonitroethane results :

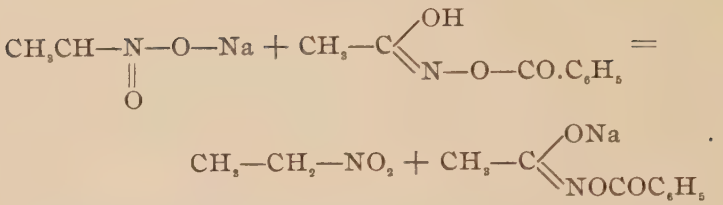
$$CH_3—CH=\underset{\underset{O}{\|}}{N}—O—Na + C_6H_5—COCl =$$

$$CH_3—CH=\underset{\underset{O}{\|}}{N}—O—CO.C_6H_5 + NaCl.$$

This substance cannot be isolated, but is immediately converted by intramolecular oxidation into the benzoyl ester of acethydroxamic acid,

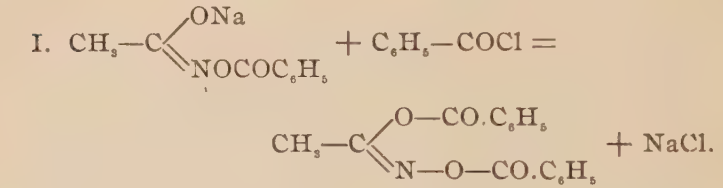
$$CH_3—CH=\underset{\underset{O}{\|}}{N}—O—CO.C_6H_5 \rightarrow CH_3—C\begin{matrix}OH\\\diagdown\\\diagup\\N—O—CO.C_6H_5\end{matrix}$$

Being a stronger acid than isonitroethane, it immediately reacts with the isonitroparaffin salt, regenerating nitroethane, and forming the sodium salt of the benzoyl ester of acethydroxamic acid,

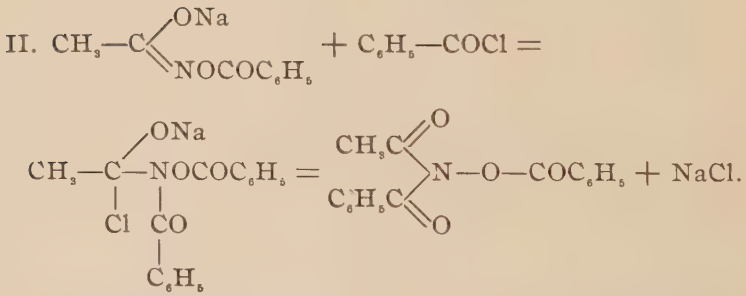


In the presence of benzoyl chloride, this salt reacts just as the synthetic salt was found to act, namely, in two ways, by addition; and by direct replacement, forming dibenzoylacethydroximic acid, and α-benzoyl-β-acetylbenzoylhydroxylamine:

I.



II.



2. *The Action of Chlorcarbonic Ether on Sodium Isonitroethane.*

This reaction has not been studied as thoroughly as the action of benzoyl chloride on sodium isonitroethane. The evolution of large amounts of carbon dioxide introduces a complication which was not foreseen, and although the resulting neutral oil contains derivatives of acethydroxamic acid, it has not been found possible to determine the exact nature of these substances.

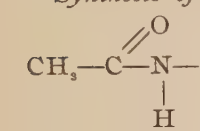
22.3 grams of chlorcarbonic ether were allowed to act on 20 grams of sodium isonitroethane, suspended in 120 grams of

absolute ether; 3.2 grams of carbon dioxide were evolved, and a residue remained which weighed 16.9 grams, and was composed of sodium chloride (66 per cent.), sodium carbonate, and some sodium nitrate. The ether gave, on evaporation, 11.2 grams of reddish, neutral oil. A loss of material had occurred amounting to 11 grams; this was due chiefly to nitroethane, and amounts to a little more than half of the sodium nitroethane used.

Properties of the Neutral Oil.—It is sparingly soluble in water. On heating a few drops with sodium hydroxide and acidifying with dilute sulphuric acid, an evolution of carbon dioxide occurred, and ferric chloride gave an intense cherry-red color reaction, identical with the test given by acethydroxamic acid. When alkalies are added to the oil, the red color characteristic of salts of ethylnitrolic acid is produced; this disappears on acidifying, and is regenerated by fresh alkali.

After standing for several weeks, the oil showed no signs of solidifying. It suffers considerable decomposition when distilled even under diminished pressure. When distilled at ordinary pressure, a portion passes over below 170°; the remainder between 200° and 230°. Carbon dioxide is evolved, and the distillate possesses an intense odor of isocyanate. A few drops of the higher-boiling fraction, heated with alkali, gave, on acidifying, an intense reaction with ferric chloride; this shows that the derivatives of acethydroxamic acid distilled, at least in part, without decomposition.

Synthesis of the Carbethoxyl Ester of Acethydroxamic Acid,



$CH_3—C(=O)—N(H)—O—CO_2C_2H_5$.—It was expected that the action of chlorcarbonic ether on sodium isonitroethane would give results corresponding to those obtained by the action of benzoyl chloride. It was necessary, therefore, to become familiar with the carbethoxy derivatives of acethydroxamic acid, and of ethylnitrolic acid. These have been prepared synthetically.

Six grams of acethydroxamic acid were dissolved in a few

cubic centimeters of cold water, and, after neutralizing with one molecule of potassium hydroxide, one molecule of chlorcarbonic ether was added. In a few minutes the reaction was complete; the clear solution was extracted with ether, the ether dried with calcium chloride, and partially distilled. The remainder, poured into an evaporating-dish, left, on evaporation, a snow-white crystalline mass, which, after drying on a clay plate to remove traces of chlorcarbonic ether, weighed 4.1 grams. Crystallized from ether and ligroïn (40°–60°), it separates in long, flat needles, with a shining, pearly luster, and melts at 71°–72°.

0.2700 gram gave 0.4039 gram CO_2, and 0.1507 gram H_2O.
0.1875 gram gave 15.2 cc. N_2 at 13°.5 and 756.4 mm.

	Theory for $C_5H_9NO_4$.	Found.
C	40.81	40.79
H	6.12	6.20
N	9.52	9.53

Properties of the Carbethoxyl Ester of Acethydroxamic Acid.—It is readily soluble in ether, alcohol, and water, soluble in benzol, and chloroform, almost insoluble in ligroïn. A water solution, when first prepared, gives no reaction with ferric chloride, but on standing several hours it shows an intense color reaction. It is readily decomposed by alkalies, and alkaline carbonates, acethydroxamic acid being formed. Towards acids it is much more stable.

Its behavior on distillation resembles, in some respects, the behavior of the neutral oil obtained by the action of chlorcarbonic ether on sodium isonitroethane; carbon dioxide is evolved, an intense odor of isocyanate is observed, and a pale yellow oil distils between 180°–220°.

Synthesis of the Carbethoxyl Ester of Ethylnitrolic Acid, $CH_3—C(NO_2)=N—O—CO_2C_2H_5$.—2.4 grams of the ethylnitrolic acid, prepared from nitroethane, were dissolved in 25 cc. of water; 0.9 gram of potassium hydroxide, and 2.5 grams of chlorcarbonic ether were added. The red color of the solution soon disappeared, and a yellow oil separated.

The solution and yellow oil were extracted with ether, the ether dried with calcium chloride, and distilled; 2.1 grams of the oil were obtained by distillation at reduced pressure, boiling at 143°–144° under 17 mm.

0.1720 gram gave 0.2187 gram CO_2, and 0.0719 gram H_2O.

	Theory for $C_5H_8N_2O_5$.	Found.
C	34.09	34.67
H	4.54	4.64

Properties.—It is a pale yellow oil, slightly soluble in water. Boiling water decomposes it, liberating carbon dioxide, and forming ethylnitrolic acid and its decomposition-products. In the presence of alkalies, it is readily decomposed, an intense red solution of salts of ethylnitrolic acid being formed. It boils at ordinary pressures, with considerable decomposition, at 210°–215°.

The presence of this substance in the neutral oil obtained by the action of chlorcarbonic ether on sodium nitroethane, accounts for the formation of salts of ethylnitrolic acid, on treating this oil with alkalies.

3. *The Action of Benzoyl Chloride on Sodium Isonitromethane.*

This reaction still presents difficulties, which have not been overcome. The action seems to proceed in a different manner, depending upon the kind of salt used, that is, whether the alcoholate, $CH_2{=}NONa,C_2H_5OH$, or the alcohol-free salt is

$$\begin{matrix} & \| \\ & O \end{matrix}$$

used.

In all cases, the chief product of the reaction is a neutral oil.

20 grams of the sodium isonitromethane[1] (alcohol-free) and 33

[1] A curious observation in this connection with nitromethane may be mentioned here. Kahlbaum's nitromethane was used, and its purity established by distillation. It was perfectly transparent, and free from color when first obtained; but, on exposure to the light for some time, it gradually assumed a pale yellow tinge, and an odor identical with that of *prussic acid* was noticed. Could this have been due to the formation of fulminic acid, H—O—N=C, by oxidation:

$$H_3C{-}NO_2{+}H_2O = H_3CN\begin{matrix} \| \\ O \end{matrix}\!\!<\!\!\begin{matrix} OH \\ OH \end{matrix} = H_2C{=}N\begin{matrix} OH \\ \| \\ O \end{matrix}{+}H_2O\,?$$

This isonitromethane, by intramolecular oxidation, could yield formhydroximic acid, and this, by loss of water, fulminic acid:

$$H_2C{=}N\begin{matrix} OH \\ \| \\ O \end{matrix} = HC\!<\!\!\begin{matrix} OH \\ NOH \end{matrix} = C{=}N{-}OH{+}H_2O.$$

grams of benzoyl chloride in 180 grams of absolute ether, gave 19.8 grams of reddish, neutral oil. The solid residue weighed 17.2 grams, and contained, in addition to sodium chloride, a considerable quantity of sodium benzoate. The sodium bicarbonate, and sodium hydroxide extracts gave 5.3 grams of benzoic acid. A loss, therefore, of 10.7 grams of material had occurred, which was due to regenerated nitromethane.

Properties of the Neutral Oil.—The oil could not be solidified. Complete decomposition ensued on attempting to distil it, even at reduced pressure; benzoic acid, and isocyanate were formed. Concentrated hydrochloric acid decomposed it, forming large quantities of benzoic acid (3 grams of oil gave 2.6 grams of benzoic acid), small amounts of formic acid (identified as lead salt), and some hydroxylamine hydrochloride (identified as acetoxime). When heated with dilute alkalies, it suffers decomposition; benzoic acid is deposited on acidifying, and the solution gives an intense reaction with ferric chloride, identical with the color reaction obtained with formhydroxamic acid, $H—C\begin{matrix}=O\\ \diagdown NHOH\end{matrix}$, which has been synthetically prepared, and will be described later.

Behavior towards Alcoholic Potash.—6 grams of this neutral oil, treated with alcoholic potash in the manner described in connection with the neutral oil obtained from nitroethane, gave 3.2 grams of potassium benzoate, 2.5 grams of ethyl benzoate, 1 gram of benzoic acid, and 0.3 gram of the benzoyl ester of formhydroxamic acid, $H—C\begin{matrix}=O\\ \diagdown NHOCO.C_6H_5\end{matrix}$. The mixture of benzoic acid and the benzoyl ester of formhydroxamic acid extracted from the acidified alcoholic solution by ether was treated with boiling ligroïn to remove benzoic acid, and the remaining benzoyl ester of formhydroxamic acid purified by recrystallizing from ether and ligroïn. It separated in transparent crystals, melting at 76°–77°, identical with the crystals of this substance prepared synthetically from formhydroxamic acid and benzoyl chloride, which will be described in connection with formhydroxamic acid.

The formation of this substance, by the action of alcoholic potash on the neutral oil, confirms the presence of the benzoyl ester of benzoylformhydroxamic acid in the oil. It is, therefore, evident that the action of benzoyl chloride on sodium nitromethane proceeds, at least in part, according to the following equations:

$$H_2C{=}N(=O){-}ONa + C_6H_5{-}COCl = H_2C{=}N(=O){-}O{-}CO.C_6H_5$$

By oxidation this is converted into the benzoyl ester o formhydroxamic acid, $H{-}C(OH){=}NOCOC_6H_5$, which decomposes sodium isonitromethane, forming the sodium salt of the benzoyl ester of formhydroxamic acid, and liberating nitromethane:

$$HC(OH){=}NOCOC_6H_5 + CH_2{=}N(=O)ONa = H{-}C(ONa){=}NOCOC_6H_5 + CH_3{-}NO_2.$$

This salt then reacts with benzoyl chloride exclusively by direct replacement:

$$H{-}C(O{-}Na){=}NOCOC_2H_5 + C_6H_5COCl = H{-}C(OCOC_6H_5){=}N{-}O{-}COC_6H_5,$$

forming the benzoyl ester of benzoylformhydroxamic acid. That addition does not take place in this reaction is proved by the fact that in no case has it been possible to obtain the benzoyl ester of benzhydroxamic acid, $C_6H_5CO{-}NH{-}O{-}COC_6H_5$, as one of the decomposition-products of the neutral oil.

Synthesis of Formhydroxamic Acid, $H{-}C(=O){-}N(H){-}O{-}H$, *and its Benzoyl Derivatives.*

It was expected that the chief products of the action of ben-

zoyl chloride on sodium isonitromethane would be benzoyl derivatives of formhydroxamic acid.

In order to become familiar with the properties of these substances, it was necessary first to prepare synthetically formhydroxamic acid, the simplest of the hydroxamic acids.

Formhydroxamic Acid, $H-\overset{\overset{O}{\|}}{C}-N(\overset{\overset{H}{|}}{})-OH$.—A brief mention is made by Miolati[1] of a copper salt of formhydroxamic acid, but he does not describe any attempts to isolate the free acid. After several trials, the following method of preparation has been found to be the most satisfactory :

30 grams of hydroxylamine hydrochloride were dissolved in 150 cc. of boiling methyl alcohol, and to this solution, still warm, a solution of sodium methylate, containing 9.9 grams of sodium, was added. After mixing, the flask was cooled, and finally allowed to stand in a freezing-mixture for some time. The sodium chloride was filtered off, and the alcoholic solution of hydroxylamine distilled at reduced pressure, until two-thirds of the alcohol had distilled over.

After removing a small amount of sodium chloride, which had been deposited during the distillation, by filtering through glass wool, the solution was cooled to 0°, and 31 grams of formic ether added directly. A slight elevation in temperature was observed, which was moderated by shaking, and cooling with running water. After standing for several hours at the temperature of the room, the mixture was placed in a glass evaporating-dish, and the methyl alcohol removed by evaporating in a vacuum-desiccator. 20 grams of crystalline material, containing some oil, and a slight amount of sodium chloride remained. The oil was removed by pressing the residue on a clay plate. Thus 17.9 grams of almost pure formhydroxamic acid were obtained, which was freed from the small quantity of sodium chloride by dissolving in pure ethyl acetate (free from acetic acid and water), heated to a temperature near its boiling-point. If

[1] Ber. d. chem. Ges., **25**, 703.

heated too long, or too high, much decomposition results.

On cooling, pure formhydroxamic acid, melting at 81°–82°, separated in large, thin, transparent plates, with a brilliant, pearly luster, and striated surfaces.

0.1890 gram gave 0.1359 gram CO_2, and 0.0847 gram H_2O.

0.1765 gram gave 35.8 cc. N_2 at 17° and 743.4 mm.

	Theory for $H-C\overset{O}{\diagdown\!\!\diagup NHOH}$.	Found.
C	19.67	19.60
H	4.91	4.98
N	22.95	23.09

Properties of Formhydroxamic Acid.—It is insoluble in chloroform, ligroïn, and benzol; very slightly soluble in ether; readily soluble in alcohol, and water. It is dissolved by warm acetone, and is deposited on cooling in groups of thick crystals. On standing in contact with acetone, however, these crystals redissolve, and suffer a decomposition, the nature of which has not been fully determined. If perfectly pure formhydroxamic acid is required, it can be prepared best by using pure hydroxylamine, obtained by distillation according to the method of Lobry de Bruyn, instead of the concentrated alcoholic solution containing sodium chloride. A water solution of formhydroxamic acid, even in the presence of considerable mineral acid, gives an intense cherry-red color reaction with ferric chloride, differing very slightly in tint from the color obtained with acethydroxamic acid.

The pure acid is quite stable, is not hygroscopic, and can be kept in open vessels without decomposition; in closed tubes, it soon undergoes decomposition. When heated to a temperature slightly above its melting-point, it explodes with a sudden puff, sending forth a cloud of vapor, possessing the peculiar odor of hydroxylamine. This decomposition seems to be due to a dissociation into carbon monoxide and free hydroxylamine:

$$H-C\overset{O}{\diagdown\!\!\diagup NHOH} = CO + H_2NOH.$$

The stability of this substance is best explained by assign-

ing to it the oxam formula, H—C(=O)NHOH ; if the oxime form, H—C(OH)=NOH, were correct, this substance would lose water spontaneously, and give fulminic acid :

$$HO\diagdown \atop H\diagup \!\!> C{=}NOH = H_2O + C{\equiv}NOH,$$

just as the oxime of formyl chloride, $Cl\diagdown \atop H\diagup \!\!> C{=}NOH$, was found to lose hydrochloric acid. It is, therefore, very probable, that the hydroxamic acids in the free state are constituted according to the oxam, and not according to the oxime type.[1]

Sodium Salt.—A sodium salt is formed by adding to an alcoholic solution of the acid one molecule of sodium ethylate. The alcohol must be absolute, otherwise the salt will separate as a gummy mass. A precipitate is first formed, which redissolves on adding the entire amount of sodium ethylate. This is probably an acid salt. From the alcoholic solution, the sodium salt is precipitated by adding absolute ether as a fine, white powder. The filtration and washing must be carried out very rapidly, as the salt is extremely hygroscopic. No analysis was made. Heated on a spatula, the salt explodes with a sharp puff, and a yellow flame. Salts are precipitated from its water solution by copper acetate, mercuric chloride, and lead acetate.

The copper salt is a dark green powder. The lead salt separates as a white, crystalline powder, which explodes on heating. The mercury salt, a deep yellow powder, explodes by percussion and on heating.

The Action of Benzoyl Chloride on the Salts of Formhydroxamic Acid.

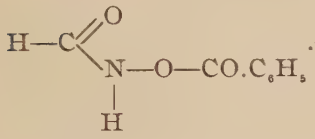
To a solution of 10 grams of formhydroxamic acid in 50

[1] The study of formhydroxamic acid, and its derivatives, especially in their relation to and conversion into fulminic acid and its esters, RON=C, will be continued in this laboratory.—J. U. Nef.

grams of cold water (5°), a solution of 6.5 grams of sodium hydroxide in 25 grams of water was added, and then benzoyl chloride, in small portions, until 23.3 grams were used. During the reaction the temperature was kept at 5°, and the flask shaken from time to time. A thick, gummy mass separated, and floated on the surface of the water. After shaking for ten minutes, the mixture was transferred to a separatory-funnel, and extracted with ether. Neutral and acid products were obtained by shaking the ether-extract first with a solution of sodium bicarbonate, then with a solution of sodium hydroxide. The remaining ether contained the neutral portion. The original water solution, after extraction with ether, gave an intense reaction with ferric chloride, showing the presence of large amounts of unchanged formhydroxamic acid.

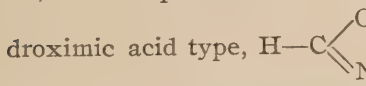
Soluble in Sodium Bicarbonate.

Benzoyl Ester of Formhydroxamic Acid,

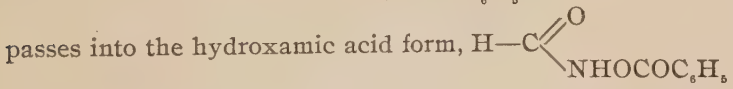


.—On acidifying the solution in sodium bicarbonate with dilute sulphuric acid, a colorless oil was formed. This was taken up by ether, the ether dried with calcium chloride, and evaporated; 7 grams of solid residue (no oil!) remained.

It is possible that in this case, also, two forms exist; the oil, which separated on acidifying, may correspond to the hydroximic acid type,



, which readily passes into the hydroxamic acid form,



.

A small amount of benzoic acid was removed by boiling ligroïn, and the remaining solid, 5.5 grams, which melted at 55°–60°, was dissolved in 50 cc. of absolute ether. On cooling, it crystallized in well developed, prismatic crystals, melting at 76°.5–77°.5. By addition of ligroïn it is completely precipitated from ether solution.

0.1250 gram gave 0.2662 gram CO_2, and 0.0487 gram H_2O.
0.1710 gram gave 12.9 cc. N_2 at 21° and 753 mm.

	Theory for $C_8H_7NO_3$.	Found.
C	58.18	58.08
H	4.24	4.32
N	8.48	8.54

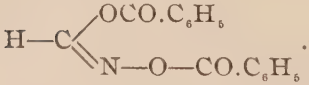
Properties of the Benzoyl Ester of Formhydroxamic Acid.— It is readily soluble in alcohol, less soluble in ether, almost insoluble in ligroïn, and sparingly soluble in water. By sodium hydroxide it is decomposed, slowly in the cold, readily on warming, into formhydroxamic acid and benzoic acid. Heat decomposes it; benzoic acid distils, and an intense odor of isocyanate is observed. The substance is identical with the benzoyl ester of formhydroxamic acid, obtained from nitromethane.

Soluble in Sodium Hydroxide.

Two grams of the benzoyl ester of benzhydroxamic acid, $C_6H_5CONHOCOC_6H_5$, (melting at 159°–160°), were obtained from the acidified solutions. Its formation is to be accounted for by the partial decomposition of formhydroxamic acid into carbon monoxide and hydroxylamine.

Neutral Portion.

Benzoyl Ester of Benzoylformhydroximic Acid,[1]

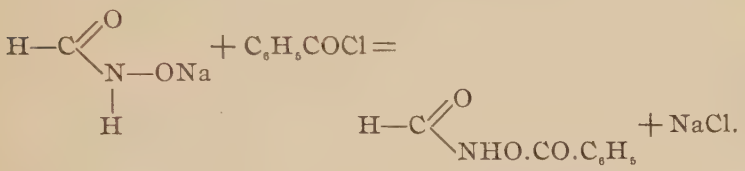


.—Most of the ether was removed by distillation. On pouring the remainder into an evaporating-dish, 7.5 grams of crystalline solid separated. Recrystallized from warm ether and ligroïn, it was obtained in delicate, colorless needles, melting at 109°–111°.

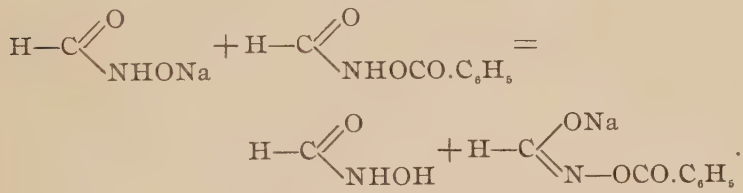
0.1407 gram gave 0.3443 gram CO_2, and 0.0553 gram H_2O.
0.2539 gram gave 12.2 cc. N_2 at 25° and 745 mm.

	Theory for $C_{15}H_{11}NO_4$.	Found.
C	66.91	66.74
H	4.08	4.36
N	5.20	5.28

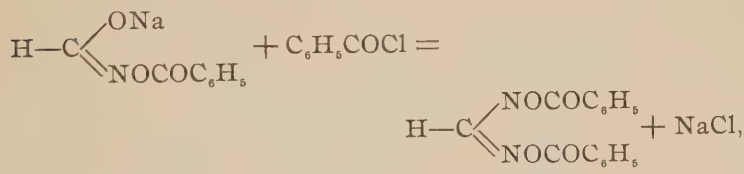
Properties. — It is quite readily soluble in warm ether, and sparingly in cold ether, slightly soluble in warm ligroïn, and insoluble in water. It is insoluble in alkalies, but is decomposed by them, more readily on warming than in the cold. On acidifying, benzoic acid separates, and the solution gives an intense reaction with ferric chloride for formhydroxamic acid. The reaction may be represented by the following equations:



The benzoyl ester of formhydroxamic acid being a stronger acid than formhydroxamic acid, decomposes the sodium salt of the latter, setting free formhydroxamic acid,



This sodium salt then reacts with benzoyl chloride,

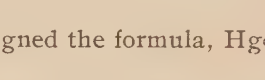


to give the benzoyl ester of benzoylformhydroximic acid.

Experiments with the Mercury Salt Obtained by the Action of Mercuric Chloride on Sodium Isonitromethane.

83 grams of sodium isonitromethane were dissolved in water, and, after cooling to 0°, a cold solution containing 121 grams of mercuric chloride was added. After standing two days, the white precipitate, which was at first deposited, be-

came yellow; it was boiled twice with water, filtered, and dried carefully on a clay plate. The product weighed 105 grams.

Many fruitless experiments were carried out with the salt and alkyl iodides. The mercury salt was supposed to be a basic mercury salt of carbon dioxide oxime, H—O—N=C=O, to which Nef assigned the formula,  . It was hoped that esters of this acid, R—O—N=CO, would result.

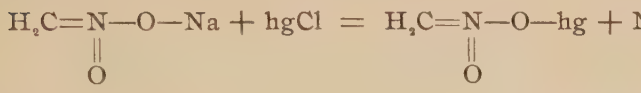
A peculiar odor resembling that of prussic acid was observed by Nef, on treating this salt with dilute hydrochloric acid. In order to determine the nature of this substance, 10 grams of the mercury salt were heated with the calculated amount of dilute hydrochloric acid, and an attempt made to distil the volatile substance, and collect it in a well-cooled receiver. The yellow color of the salt disappeared, and a gray residue remained, weighing 3 grams. When a small portion of this residue was heated on a spatula, it exploded exactly like mercuric fulminate. It was redissolved in a solution of potassium cyanide, and precipitated, by adding dilute nitric acid, as a crystalline powder, identical with mercuric fulminate.

The original yellow salt is also soluble in potassium cyanide, but, if dilute nitric acid is added rapidly, not a trace of fulminate is obtained. It is, however, possible, by adding nitric acid drop by drop, to obtain mercuric fulminate from the solution of the salt in potassium cyanide.

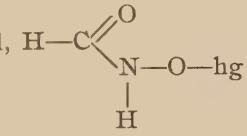
The peculiar odor observed on treating the salt with dilute hydrochloric acid is due, therefore, to small quantities of formyl chloride oxime, .

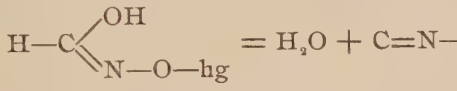
In view of the experiments with acid chlorides and isonitroparaffin salts, which have led, in all cases, to the formation of hydroxamic acid derivatives, it seems likely that, in the action of mercuric chloride on sodium isonitromethane, derivatives of formhydroxamic acid may be formed, as intermediate prod-

ucts in the synthesis of fulminates, discovered by Nef.[1] Thus,[2]

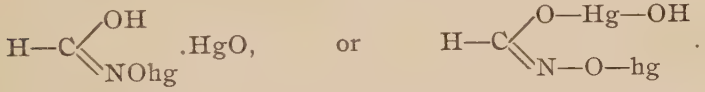


By oxidation,

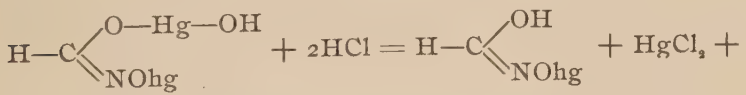
This salt of a hydroximic acid, before it can readjust itself to form a salt of a hydroxamic acid,  , loses water, giving rise to mercuric fulminate,

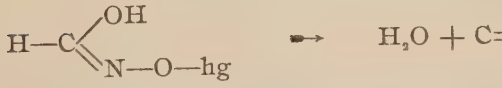


At the same time, by the further action of mercuric chloride, a basic mercury salt of formhydroximic acid results,



It is evident that on treating this basic salt with dilute hydrochloric acid, mercuric fulminate must be formed.





The analysis of the yellow mercury salt, made by Nef, agrees almost exactly with the theory for a basic mercury salt of formhydroxamic acid.

[1] Ann. Chem. (Liebig), **280**, 270. [2] hg represents a half atom of bivalent mercury.

	Theory for $H-C(=NOhg)-O-Hg-OH$.	Found.
C	3.2	3.34
H	0.53	0.305
N	3.7	4.04
Hg	79.7	80.31

This interpretation is offered tentatively. It may be mentioned that a yellow mercury salt has been obtained by the action of mercuric chloride on the sodium salt of formhydroxamic acid, which resembles, in many respects, the peculiar salt described above. Both explode violently on heating, and by percussion.

The above experiments prove, in any case, that the yellow basic salts obtained from nitromethane cannot be derivatives of carbon dioxide oxime, as was considered probable by Nef; their behavior towards sodium amalgam, and other reagents, makes it improbable that they are basic fulminates. Their conversion into fulminates, as shown above, makes it possible to convert sodium isonitromethane almost quantitatively into mercuric fulminate.

Concerning the Formula of the Salts of the Nitroparaffins.

In assigning to the isonitroparaffins the open formula, $R-\underset{|}{\overset{H}{C}}=\underset{||}{\overset{O}{N}}-OH$, and excluding the ring grouping of Hantzsch, $R-\overset{H}{\underset{|}{C}}(<\overset{O}{\underset{}{}})-N-OH$,[1] it was pointed out by Nef[2], that the latter formula does not explain the peculiar property, which these bodies possess, of undergoing intramolecular oxidation.

Many instances can be cited in which formulæ containing ring groupings have been assumed arbitrarily for which there is no experimental evidence. As examples of this kind, the following may be mentioned:

[1] Ber. d. chem. Ges., **29**, 699, 2251. [2] *Ibid.*, **29**, 1218.

Nitrous oxide, $N{=}N$ (O) instead of $N{\equiv}N{=}O$.

Azoxy bodies, $R{-}N{=}NR$ (O) instead of $R{-}N{=}N{-}R$ (=O).

Nitric acid, $HO{-}N{<}^{O}_{O}$ instead of $HO{-}N{<}^{O}_{O}$.

Nitramine salts, $R{-}N{-}NOM$ (O) instead of $R{-}N{=}NOM$ (=O).

Isonitramine salt, $R{-}N{-}NOM$ (O) instead of $R{-}N{=}NOM$ (=O).

The oxidation reactions may be grouped into two classes:

I. Cases in which the oxidation extends only to the adjacent carbon atom:

1. $R{-}CH{=}N{-}O{-}Ac$ (or M) (=O) $\rightarrow R{-}C{<}^{OH}_{N{-}O{-}Ac\,(or\ M)}$

2. $2R{-}CH{=}N{-}O{-}H$ (=O) $\rightarrow 2R{-}C{<}^{H}_{O} + N_2O + H_2O$.

II. Cases in which the oxidation extends to carbon atoms not adjacent to the nitrogen atom:

$$R{-}\overset{R}{\underset{}{C}}{=}N{-}OR\ (=O) \rightarrow R{-}\overset{R}{\underset{}{C}}{=}NOH + R{-}C{<}^{O}_{H}.$$

(an aldehyde.)

The oxidations belonging to Class I include all of the cases described in this paper; the formation of fulminates from nitromethane sodium;[1] and the peculiar decomposition of the salts of the nitroparaffins into an aldehyde (or ketone) and

[1] Ann. Chem. (Liebig), **280**, 263.

nitrous oxide, by the action of dilute acid, observed by Nef.[1]

Examples of the second class have been described by Nef.[2] Dinitroethane silver, $CH_3—\underset{\underset{NO_2}{|}}{C}=N—O—Ag$, on treatment with alkyl iodides, gives results which can only be explained by admitting the formation of an ester, $CH_3—\underset{\underset{NO_2}{|}}{C}=N—O—R$, which then decomposes, giving an aldehyde, and ethylnitrolic acid,

$$CH_3—\underset{\underset{NO_2}{|}}{C}=N—O—CH_2—R \rightarrow CH_3—\underset{\underset{NO_2}{|}}{C}=N—O—H + R—C\overset{O}{\underset{H}{<}}$$

in the manner described by Nef. Another instance is found in the ethyl ester of fulminuric acid,

$$N\equiv C—\underset{\underset{C=O.NH_2}{|}}{C}=N—O—C_2H_5 \rightarrow$$

$$N\equiv C—\underset{\underset{CONH_2}{|}}{C}=N—O—H + CH_3—C\overset{O}{\underset{H}{<}},$$

which, on boiling with water, gives acetic aldehyde, and cyanisonitrosoacetamide.

It is impossible to see how these reactions are to be interpreted, if the ring grouping is adhered to.

II. Carbethoxyhydroxamic Acid (Oxyurethane), $C_2H_5O—C\overset{O}{<}_{NHOH}$, and its Alkyl and Acyl Derivatives.

In connection with the study of the mercury salt described above, attempts were made to obtain derivatives of the oxime of carbon dioxide, HO—N=C=O, from the salts and esters

[1] Ann. Chem. (Liebig), **280**, 266.
[2] *Ibid.*, **280**, 266.

of carbethoxyhydroxamic acid. If the salts possessed the form assigned by Lossen to the hydroxamic acids, $C_2H_5O—C(OH)=N—OM$, it seemed possible that under certain conditions they would lose alcohol, and give rise to salts of the oxime of carbon dioxide. Many attempts were made to remove this alcohol, but without success.

The monoalkyl esters of carbethoxyhydroxamic acid were then prepared, $C_2H_5O—C(=O)—NHOR$ ($R = CH_3$, C_2H_5, C_7H_7), and preliminary experiments with these compounds have been carried out. It was expected that under the influence of phosphorus pentachloride, these esters would be decomposed, yielding hydrochloric acid, an alkyl chloride, and esters of the oxime of carbon dioxide, R—ON=C=O. These esters have not yet been isolated, but are undoubtedly formed in this way.

Carbethoxyhydroxamic Acid (*Oxyurethane*), $C_2H_5O—C(=O)—NHOH$.—This substance was first prepared by Hantzsch,[1] who obtained it by the action of hydroxylamine, in water solution, on chlorcarbonic ether, in the presence of sodium carbonate. The following modification of this method has been used, and found to give more satisfactory yields :

19.5 grams of hydroxylamine hydrochloride were finely powdered, and placed in a flask with 38 grams of powdered dry potassium carbonate. Enough ether was added to more than cover the mixture, and a few cubic centimeters of water. 30 grams of chlorcarbonic ether were then poured into the flask, a small portion at a time ; the flask was cooled, and shaken until the violent solution of carbon dioxide moderated, and permitted the addition of another portion of chlorcarbonic ether. When the entire amount had been used, the flask was allowed to stand, being shaken from time to time, until the evolution of carbon dioxide ceased. The potassium

[1] Ber. d. chem. Ges., **27**, 1254.

chloride was removed by filtration, the ether was washed once with water, dried with dehydrated sodium sulphate, and the ether distilled; 26 grams of carbethoxyhydroxamic acid were obtained, equal to 89.6 per cent. of the theoretical yield.

Properties.—Prepared in this way it is identical with the oxyurethane described by Hantzsch.[1] It is a thick, colorless liquid, extremely soluble in water, and gives with ferric chloride an intense color reaction. On distillation, it was almost completely decomposed; at 180°–185° a colorless liquid distilled, which, on cooling, solidified to a mass of large, transparent plates, melting at 49°–50°. These were found to be urethane, $O{=}C\begin{matrix}NH_2\\OC_2H_5\end{matrix}$, (melting-point 49°–51°, boiling-point 184°).

Sodium Salt of Carbethoxyhydroxamic Acid, $C_2H_5{-}O{-}C\begin{matrix}O\\NHONa\end{matrix}$. H_2O.—By adding sodium ethylate to an alcoholic solution of the acid, a sodium salt is precipitated as a white, crystalline powder, which detonates when heated to 110°.

0.2474 gram gave 0.1288 gram of Na_2SO_4.

0.2974 gram gave 0.1470 gram of Na_2SO_4.

	Theory for $C_3H_6NO_3Na + H_2O$.	Found. I.	II.
Na	15.86	16.8	16.0

This salt is readily soluble in water, and its solution reduces silver nitrate in the cold, and Fehling's solution on warming.

The Action of Methyl Iodide on Salts of Carbethoxyhydroxamic Acid.

To a solution of 29 grams of carbethoxyhydroxamic acid in methyl alcohol, a solution of 15.4 grams of potassium hydroxide in methyl alcohol, and 42 grams of methyl iodide were added. The separation of potassium iodide commenced at once, and it became necessary to cool the flask to prevent too great an elevation of temperature. After standing twenty-

[1] *Loc. cit.*

four hours, the potassium iodide was removed, and the methyl alcohol distilled under reduced pressure. The oil which remained, was dissolved in ether, and separated into neutral and acid portions by extracting the ether solution with dilute sodium hydroxide.

Soluble in Sodium Hydroxide.

Methyl Ester of Carbethoxyhydroxamic Acid, $C_2H_5O—C(=O)—NHOCH_3$.—After acidifying the alkaline extract with dilute sulphuric acid, it was shaken out with ether, the ether dried and distilled. 9.2 grams of colorless liquid, boiling at 186°–188°, were obtained.

0.1372 gram gave 0.2047 gram CO_2, and 0.0953 gram H_2O.

0.2092 gram gave 21.7 cc. N_2 at 17° and 749.1 mm.

	Theory for $C_4H_9NO_3$.	Found.
C	40.33	40.61
H	7.56	7.70
N	11.76	11.90

Properties.—It is readily soluble in ether, alcohol, and water. When perfectly pure, it gives no reaction with ferric chloride, but traces of carbethoxyhydroxamic acid are sometimes present in the acid portion, and are carried over with the oil. In this case a reaction with ferric chloride is obtained, and the methyl ester is rendered impure by the presence of traces of urethane.

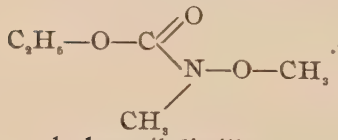
Decomposition by Concentrated Hydrochloric Acid.—1.4 grams of the methyl ester were heated with 10 cc. of concentrated acid in a sealed tube for an hour. On opening the tube, carbon dioxide and ethyl chloride escaped. The acid solution, evaporated to dryness on a water-bath, gave a crystalline residue, which dissolved completely in absolute alcohol. It was precipitated by absolute ether in white, crystalline flakes, melting at 148°–149°, identical in every respect with α-methylhydroxylamine hydrochloride, $CH_3ONH_2.HCl$, which melts at 149°.

0.0538 gram gave 0.0917 gram AgCl.

	Theory for CH_3ONH_2HCl.	Found.
Cl	42.51	42.46

Neutral Portion.

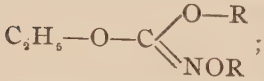
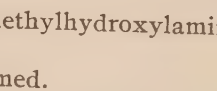
α-Methyl-β-Methylcarbethoxyhydroxylamine,



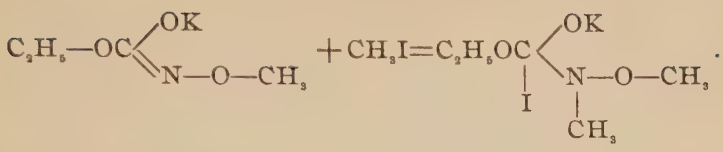
.—When the ether had passed off, a colorless oil distilled at 150°–155°, weighing 4 grams. The neutral portion is formed in larger amounts when 2 molecules of potassium hydroxide, and 2 molecules of methyl iodide, are used; thus 22.5 grams of carbethoxyhydroxamic acid, 24 grams of potassium hydroxide, and 63 grams of methyl iodide, gave 2 grams of acid oil, methyl ester of carbethoxyhydroxamic acid, boiling at 186°–188°, and 10.5 grams of neutral oil. In all cases considerable decomposition occurs.

A nitrogen determination showed that the oil was impure. 0.2410 gram (150°–153°) gave 19 cc. N_2 at 19° and 742 mm.

	Theory for $C_5H_{11}NO_3$.	Found.
N	10.52	8.88

The nature of this impurity has not been determined. It was at first expected that the neutral oil would contain alkyl derivatives of the carbethoxyhydroxamic acid of the form,  ; but the decomposition of the oil by concentrated hydrochloric acid shows that the oil consists chiefly of α-methyl-β-methylcarbethoxyhydroxylamine, for not α-methylhydroxylamine hydrochloride, CH_3ONH_2HCl, but α-dimethylhydroxylamine hydrochloride,  . HCl is formed.

In order to explain this reaction, we must assume that the alkyl iodide acts with the potassium salt of the methyl ester of carbethoxyhydroxamic acid by addition, and not by direct replacement.



This product then loses potassium iodide, giving rise to α-methyl-β-carbethoxymethylhydroxylamine.

Decomposition of the Neutral Oil by Concentrated Hydrochloric Acid.

α-Dimethylhydroxylamine Hydrochloride, $\begin{matrix}H\\CH_3\end{matrix}\!\!>\!N\!-\!O\!-\!CH_3.HCl$.—Two grams of the oil (boiling-point 150°–155°), were heated in a sealed tube to 100° for thirty minutes with 10 cc. of concentrated hydrochloric acid. On opening the tube, carbon dioxide and ethyl chloride escaped. A crystalline salt, weighing 0.8 gram remained on evaporating the hydrochloric acid solution to dryness on a water-bath. The salt was soluble in alcohol, and precipitated from this solution by absolute ether, in small, shining plates, melting at 115°–116°. The best method of purifying it consists in dissolving the residue in boiling chloroform, from which it crystallizes, on cooling, in long, coarse, prismatic needles, melting at 115°–116°.

0.1209 gram gave 0.1086 gram CO_2, and 0.0894 gram H_2O.
0.1980 gram gave 24.5 cc. N_2 at 20° and 750.7 mm.
0.2097 gram gave 0.3057 gram of AgCl.
0.1049 gram gave 0.1555 gram of AgCl.

	Theory for $\begin{matrix}H\\CH_3\end{matrix}\!\!>\!N\!-\!O\!-\!CH_3.HCl$.	Found.	
C	24.61	24.49	
H	8.20	8.21	
N	14.35	14.37	
Cl	36.41	35.71	36.65

Properties of α-Dimethylhydroxylamine Hydrochloride.—This salt is not hygroscopic, does not reduce ammoniacal silver nitrate; Fehling's solution is not reduced. It is quite volatile at the temperature of the water-bath, and considerable loss

occurs on evaporating its solution to dryness. The same similarity in solubility is noticed in the case of α-methylhydroxylamine and α-dimethylhydroxylamine hydrochlorides, that has been observed with the methylamine and dimethylamine hydrochloride; that is, the dimethyl derivatives in each case are soluble in chloroform, while the monomethyl derivatives are not.

α-Dimethylhydroxylamine Chlorplatinate, $(CH_3NHOCH_3)_2$. $PtCl_6$.—By adding platinic chloride, dissolved in alcohol, to an alcoholic solution of the hydrochloride, a solution of the chlorplatinate was obtained. Absolute ether precipitates the chlorplatinate as a deep orange-colored powder, melting with decomposition at 180°. It is obtained in red, prismatic crystals on recrystallizing from alcohol.

0.1341 gram gave 0.0510 gram Pt.

	Theory for $(CH_3ONHCH_3)_2PtCl_6$.	Found.
Pt	38.92	38.04

α-Dimethylhydroxylamine, $\begin{matrix} H \\ CH_3 \end{matrix}\!\!>\!N—O—CH_3$.—Two grams of the hydrochloride, 5 grams of potassium hydroxide, and 10 grams of water, were placed in a small distilling-bulb, connected with a tube containing pieces of potassium hydroxide, and heated to 80° on a water-bath. The tube was connected with a condenser, through which ice-water circulated during the distillation. The free base (1 gram) was caught in a small distilling-bulb, cooled in a freezing-mixture, and redistilled, the same precautions being taken to cool the vapor. It boiled at 42°.2–42°.6.

0.1791 gram gave 0.2548 gram CO_2, and 0.1815 gram H_2O.
0.0734 gram gave 15.4 cc. N_2 at 19° and 737.8 mm.

	Theory for $\begin{matrix} H \\ CH_3 \end{matrix}\!\!>\!N—O—CH_3$.	Found.
C	39.34	38.80
H	11.47	11.26
N	22.95	23.50

Properties of α-Dimethylhydroxylamine.—It is a colorless, extremely volatile liquid, possessing a sweet, rather unpleas-

ant basic odor, not in the least ammoniacal. It does not reduce silver nitrate or Fehling's solution. This furnishes a method for preparing the α-dialkylhydroxylamines in a state of purity, and avoids all of the difficulties encountered in their preparation from α-monoalkylhydroxylamines by the action of alkyl iodides.[1]

The study of these derivatives of carbethoxyhydroxamic acid will be continued, with a view to preparing simple and mixed α-dialkylhydroxylamines.

The Action of Ethyl Iodide on the Salts of Carbethoxyhydroxamic Acid.

Twenty grams of carbethoxyhydroxamic acid, dissolved in absolute alcohol, were treated with 10.7 grams of potassium hydroxide, and 30 grams of ethyl iodide. After standing for fifteen hours, the mixture was heated for ten minutes to a temperature of 80°–90°, and, after cooling, filtered. The residue was not pure potassium iodide, but contained some potassium nitrite, and potassium carbonate.

The alcoholic solution was diluted with water, and extracted with ether. The acid portion was removed from the ether by means of dilute sodium hydroxide; the neutral products remained dissolved in the ether.

Soluble in Sodium Hydroxide.

Ethyl Ester of Carbethoxyhydroxamic Acid, $C_2H_5—O—C(=O)NHOC_2H_5$.—After acidifying the alkaline solution, it was extracted with ether, and the ether dried with calcium chloride. On distilling, 10 grams of the acid oil were obtained, boiling at 195°–196° (95°–97° at 17 mm.).

0.1412 gram gave 0.2313 gram CO_2, and 0.1029 gram H_2O.
0.1615 gram gave 0.2651 gram CO_2, and 0.1208 gram H_2O.
0.1883 gram gave 18.5 cc. N_2 at 24° and 742.5 mm.

	Theory for $C_5H_{11}NO_3$.	Found. I.	II.	III.
C	45.11	44.67	44.77	....
H	8.27	8.09	8.30	....
N	10.52	....	....	10.82

[1] Lossen: Ann. Chem. (Liebig), **252**, 235.

Properties.—It is readily soluble in water, alcohol, and ether. Concentrated hydrochloric acid decomposes it; carbon dioxide is evolved, ethyl chloride, and α-ethylhydroxylamine hydrochloride are formed. The latter substance was precipitated from its alcoholic solution by ether in shining, pearly scales, melting at 127°–128°, which were found to be identical with α-ethylhydroxylamine hydrochloride prepared synthetically.

0.2597 gram gave 0.3825 gram AgCl.

	Theory for $C_2H_5ONH_2HCl$.	Found.
Cl	36.41	36.67

Action of Phosphorus Pentachloride on the Ethyl Ester of Carbethoxyhydroxamic Acid.—It was hoped that esters of the oxime of carbon dioxide, RON=C=O, would be formed by this means, but owing to the instability of the reaction-product, it has not been possible to decide whether esters of this form are present or not; the behavior of the product, however, seems to point to their presence.

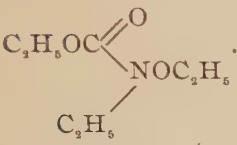
On mixing the oil with phosphorus pentachloride, the action commences at once, and is greatly facilitated by gentle heat. Hydrochloric acid and ethyl chloride are evolved in large quantities, and a yellow oil remains in the distilling-bulb, mixed with phosphorus oxychloride. An attempt was made to distil this oil; when the oxychloride had passed off, and the thermometer still stood at 110°–115°, the liquid in the distilling-bulb began to turn brown, and with an enormous evolution of heat, passed into a dark-brown, carbonaceous residue.

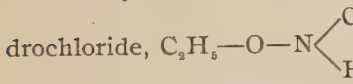
If the reaction-product was poured directly into water, without attempting to distil it, a decomposition took place, carbon dioxide was evolved, and a clear solution resulted, from which only a few drops of oil could be extracted by ether. The water solution was made strongly alkaline by adding sodium hydroxide, and distilled, the distillate passing into a receiver containing dilute hydrochloric acid.

On evaporating the acid solution, almost the calculated amount of α-ethylhydroxylamine hydrochloride was obtained. Thus 5 grams of the ethyl ester of carbethoxyhydroxamic acid

gave 2.1 grams of hydroxylamine salt instead of 2.6 grams. This shows conclusively that the ethyl chloride evolved was not produced by the ethoxy group bound to nitrogen, but must have been formed by the ethoxy group bound to carbon. The study of this reaction will be continued.

Neutral Portion.

α-Ethyl-β-Ethylcarbethoxyhydroxylamine,  .—As in the case of the neutral methyl derivative, the ethyl derivative is impure. On evaporating the ether, an oil was obtained which boiled between 160° and 180°. Owing to the small amounts of this oil which have been prepared, a separation of the mixture by fractional distillation has not been tried. Its behavior towards concentrated hydrochloric acid shows that it consists essentially of the above compound, for not α-ethylhydroxylamine, but α-diethylhydroxylamine hydrochloride is found. The substance remains on evaporating the hydrochloric acid solution to dryness as a yellow oil, soluble in alcohol, and reprecipitated by ether as an oil. The same result was obtained on precipitating from alcohol by ligroïn. With dilute sodic hydrate it gives, on warming, a strong basic odor. It does not reduce Fehling's solution or ammoniacal silver nitrate. After standing in a desiccator in the cold for several weeks, it solidified partially to a mass of long, fibrous needles, which, after recrystallization from alcohol and ether, melted at 123°–124°.

The oily salt behaves just as α-diethylhydroxylamine hydrochloride,  , which has never, until now, been obtained in the solid form.

The Action of Benzyl Chloride on Carbethoxyhydroxamic Acid Salts.

27 grams of the carbethoxyhydroxamic acid, 11.9 grams of

[1] Lossen ; Ann. Chem. (Liebig), **252**, 235.

potassium hydroxide, and 31 grams of benzyl chloride were dissolved in alcohol. Potassium chloride was deposited at once, and it was necessary to cool the flask, containing the mixture, to prevent too great a rise of temperature. After fifteen hours, the potassium chloride was removed by filtration, and after diluting the alcoholic solution with water, it was extracted with ether. The ether solution was shaken with dilute sodium hydroxide to remove acid products.

Soluble in Sodium Hydroxide.

Benzyl Ester of Carbethoxyhydroxamic Acid.

$C_2H_5—O—C(=O)—NHO—CH_2C_6H_5$.—On acidifying the alkaline extract with dilute sulphuric acid, a light, colorless oil separated, and floated on the surface of the solution. This was extracted with ether, the ether dried and distilled. The residue was subjected to distillation at reduced pressure; 17 grams of colorless oil distilled at 171°–172° under 11 mm. pressure.

0.1562 gram gave 0.3523 gram CO_2, and 0.0958 gram H_2O.
0.2245 gram gave 13.9 cc. N_2 at 18° and 754.7 mm.

	Theory for $C_{10}H_{13}NO_3$.	Found.
C	61.53	61.51
H	6.61	6.82
N	7.18	7.13

Properties.—It is a thick, colorless oil, almost insoluble in water, readily soluble in alcohol and ether. It is soluble in alkalies, and is precipitated undecomposed by acids. On distilling at ordinary pressure, it suffers partial decomposition; a slight odor of benzaldehyde was observed.

Potassium Salt.—By adding alcoholic potash to an alcoholic solution of the acid, and precipitating with ether, the salt is obtained as a white, crystalline powder. It does not fuse at 260°. Heated in a tube, it decomposes, forming volatile, aromatic oils.

Sodium Salt.—The sodium salt was prepared by the action of sodium ethylate on an alcoholic solution of the acid. This

salt is much more soluble in alcohol than the potassium salt, and is not precipitated by ether.

The alcoholic solution was evaporated in a vacuum-desiccator; a colorless liquid remained, which redissolved on adding ether, and, after scratching with a glass rod, separated as a powder.

Action of Concentrated Hydrochloric Acid on the Benzyl Ester of Carbethoxyhydroxamic Acid.

It is decomposed by this reagent slowly in the cold, more readily on warming, and α-benzylhydroxylamine hydrochloride is deposited in pearly scales, which sublime above 220°. When treated with potassium cyanate, delicate needles of the urea derivative, $OC<^{NHOC_7H_7}_{NH_2}$, melting at 138°, were obtained.

The neutral oil, formed as a bye-product in the above experiment, boiled at 190°–215° at 15 mm.; it has not been investigated.

The Action of Benzoyl Chloride on Salts of Carbethoxyhydroxamic Acid.

Benzoyl Ester of Carbethoxyhydroxamic Acid, $C_2H_5O—C(=O)NHOCO.C_6H_5$.—7.9 grams of carbethoxyhydroxamic acid were dissolved in water, and neutralized with 4.2 grams of potassium hydroxide. To this solution 10.1 grams (1 mol.) of benzoyl chloride were added. The mixture was shaken until the odor of benzoyl chloride became faint, and a colorless oil had separated. Without removing the oil, the contents of the flask were transferred to a separatory funnel, and extracted with ether. The benzoyl derivative was then extracted from the ether by means of dilute sodium hydroxide, and precipitated from this alkaline solution by means of carbon dioxide. A colorless oil separated, which was again taken up by ether. After drying and evaporating the ether, 8 grams of oil were obtained. After standing for

six months in a desiccator, this oil gave indications of solidifying, and in a few hours became a mass of soft, fibrous crystals, melting at 38°–39°.

0.3104 gram gave 18.6 cc. N_2 at 15° and 744.1 mm.

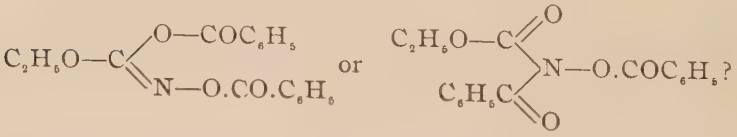
	Theory for $C_{10}H_{11}NO_4$.	Found.
N	6.69	6.89

Properties.—It can be distilled at diminished pressure, but suffers considerable decomposition; at 180°–190° and 20 mm., a colorless oil passes over, possessing an intense odor of isocyanates, and depositing crystals of benzoic acid on standing. This distillate can be dissolved in alkalies, and reprecipitated by carbon dioxide.

The solid is readily soluble in ether, alcohol, and ligroïn, almost insoluble in water. Alkalies decompose it, even in the cold, on standing for a short time, into benzoic acid, and carbethoxyhydroxamic acid.

Sodium Salt.—By the addition of sodium ethylate to an alcoholic solution of the acid, and precipitation with ether, a white salt is formed. A yellow silver salt separates on adding silver nitrate to a water solution of the sodium salt.

Dibenzoyl Derivative of Carbethoxyhydroxamic Acid,



1.5 grams of the sodium salt of the benzoyl ester of carbethoxyhydroxamic acid were suspended in absolute ether, and treated with 0.9 gram of benzoyl chloride; 1.9 grams of oil were obtained on evaporating the ether solution. This solidified partially to a mass of colorless crystals. Recrystallized from ether and ligroïn, it was obtained in transparent, prismatic crystals, melting at 72°–73°.

0.0965 gram gave 0.2301 gram CO_2, and 0.0426 gram H_2O.

0.3275 gram gave 13.4 cc. N_2 at 22° and 743 mm.

	Theory for $C_{17}H_{15}NO_5$.	Found.
C	65.17	65.03
H	4.79	4.90
N	4.47	4.55

Properties.—It is slightly soluble in warm ligroïn, readily soluble in ether, and alcohol.